

N 69 25545

NASA CR 100909

GEORGIA INSTITUTE OF TECHNOLOGY  
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Atlanta, Georgia 30332

Fifth and Sixth Semi-Annual Reports  
Research Project B-509

CHEMICAL REACTIVITY OF HYDROGEN, NITROGEN AND OXYGEN  
ATOMS AT TEMPERATURES BELOW 100°K

by

Henry A. McGee, Jr.

**CASE FILE  
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NASA Grant NGL-11-002-005 (formally Nsg 337)

Performed for

National Aeronautics and Space Administration  
Washington, D. C.

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## I. INTRODUCTION

A. Space Chemistry. - This research program is concerned with the development of chemical information at cryogenic temperatures, particularly on systems that astronomers and astrophysicists feel are important in comets and in the atmospheric and surface chemistry of the planets. This objective rather quickly resolves itself into studies of low molecular weight compounds of the four reactive elements of maximum cosmic abundance, namely hydrogen, carbon, nitrogen and oxygen.

The approach here is not one of free radical stabilization, i.e., centered upon attempts to isolate labile species in inert matrices at very low temperatures which would otherwise be chemically lost with zero activation energy. The concentrations of such species are limited to a maximum of a few tenths of a per cent (usually much less), and hence, the importance of such systems in cosmic chemistry would seem to be minimal. The matrix technique, particularly when combined with ir or epr, does, of course, provide a powerful means to study the physical and chemical properties of free radicals.

By contrast, low molecular weight species which have singlet electronic ground states, i.e., species that are highly reactive but are not free radicals, are in an altogether different category. Examples of such substances are cyclobutadiene, cyclopropanone, oxirene, diimide, ammonium ozonide, benzyne, tetrahydrofuran, and many others. One would expect such species to exhibit an activation energy for reaction, but we would also expect this energy to be unusually small. If an activation energy exists, then substances such as these may be preparable as stable cryochemical reagents and a true chemistry at very low temperatures may be developed. Since the activation energies involved in these systems are small, it will usually be necessary to maintain the compounds below some critical temperature if they are to be manipulated as stable, pure reagents. Hence, all of the common operations of chemistry must be adapted to cryogenic temperatures. A central operation in any chemical investigation is analysis. In earlier reports on this grant, the development of unique cryogenically cooled reactor-inlet attachments to the time-of-flight mass spectrometer have been described in detail. The cryogenic mass spectrometer

continues to be the key analytical tool in the approach to low temperature chemistry that is being pursued in this laboratory with three large mass spectrometers presently in use in various aspects of this NASA research program.

The best characterization of those strange nomads of space, the comets, is the so-called "dirty snowball" model of Whipple as modified by Donn and Urey.<sup>1</sup> Here the comet's nucleus is considered to be composed of frozen ices of simple compounds such as  $\text{NH}_3$ ,  $\text{H}_2\text{O}_2$ ,  $\text{C}_2\text{H}_2$ , etc., and some meteoric dust. However, it has been necessary to postulate highly energetic reactions occurring at very low temperatures in order to explain cometary phenomena observed by astronomers. It is possible, if not highly probable, that these reactions involve as yet unknown species which are stable when cold but which react vigorously upon slight warming. The search for the existence of such species and the study of their chemistry and energetics continues to be the primary objective of this NASA program. One should also recall that the atmosphere and surfaces of the Jovian planets are very cold (even Mars is much colder than earth), and hence, the equivalents of earthbound meteorology, geochemistry, and possibly other areas of geophysics in which chemistry is important, must be understood, as it applies to that particular planet, in terms of low temperature chemistry. A build-up of general knowledge in the phenomenological chemical behavior of species likely to be present will also be valuable inputs to the engineering designs of landing vehicles for both manned and unmanned explorations of the future.

B. Industrial Chemistry. - As this work has developed, we have found rather eager interest on the part of segments of the chemical process industry in many of these same sorts of reactions. These people are interested in energy storage and conversion and in chemical synthesis. Our way of life depends upon the inexpensive availability of a wide variety of chemicals in tonnage quantities, and any process or technique which offers hope of economy or variety in these syntheses is sure to attract attention. The low temperature procedures developed here represent a totally new dimension of preparative chemistry, and, since industrial chemistry is preparative chemistry, they also represent new dimensions (however embryonic) of industrial chemistry. We are

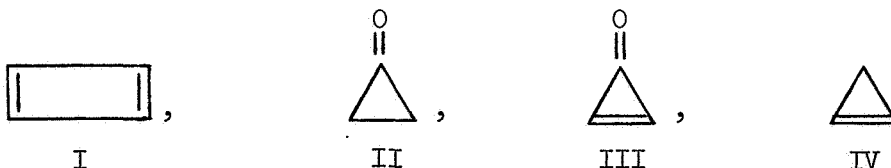
working hard toward expanding our long-time and fruitful dialogue with segments of the chemical process industry into activities of a concrete collaborative nature.

The existence of very substantial industrial interest in the research and teaching programs of this laboratory is, we think significant, and is worth bringing to the attention of NASA. Research and teaching in this laboratory are completely intermeshed and are of equal importance. Students get strong backgrounds of formal training in both engineering and in chemistry. Their thesis research in cryochemistry and kinetics seems to stretch the student in both the areas of engineering concern and in the more scientific concerns in that each involves complex problems in experimental design; each has definite and significant implications as regards generalization to large scale operation, and each has first-rate scientific merit. Not only the "space-defense" industry, but also the general chemical process industry manifests its interest in such students by their position and salary offers which are in the national upper 10 per cent for all new Ph.D.'s in science and engineering.

As a unit of a technological Institute which is beginning to realize its potential for greater contributions to the economy and well-being of the entire South, we are vitally interested in both the development of technology and in the utilization of that technology. Judging by past performance, it would appear that this NASA program can function very well in both of these regards.

## II. RESEARCH

A major part of this NASA program in space chemistry is the synthesis, energetics, and chemical characterization of low molecular weight, highly reactive compounds of C, H, N and O. Progress has occurred with cyclobutadiene(I), cyclopropanone(II), cyclopropenone(III), and cyclopropene(IV).



Compounds I, II, and III are central issues in the theory and practice of organic chemistry. They have been postulated as reaction intermediates, and their direct observation has been vigorously sought by numerous investigators for many years, but with little or no success.

The new techniques of cryochemistry are applicable to the isolation and characterization of such compounds.

A. Cyclobutadiene. - Cyclobutadiene is a highly strained cyclic dimer of acetylene<sup>2</sup> that has been directly, but not definitively, observed in only one experiment which was based on kinetic mass spectrometry in flash photolyzed cyclobutadieneirontriacetyl (CIT).<sup>3</sup> We now report the mass spectrum, ionization potential, and the indefinite free existence of condensed cyclobutadiene at very low temperatures from the pyrolysis and rapid cryo-quench of CIT. These new data, though compelling, are however, still not completely definitive, but it seems clear that any absolute identification and characterization of cyclobutadiene will demand the techniques of cryochemistry. We may also reasonably expect the preparation of cyclobutadiene as a neat cryochemical reagent provided only that the activation energies for its very facile diene reactions, although very small, are nonetheless finite.

The apparatus consists of a pyrolysis furnace mounted inside a cryogenically cooled inlet system attached to a Bendix time-of-flight mass spectrometer.<sup>4</sup> The furnace was constructed of a 5 mm OD Pyrex tube wound with Nichrome wire providing a heated length of 3.5 cm. The furnace was mounted coaxially inside an 11 mm ID monel quenching tube which was kept at  $-196^{\circ}$  and  $10^{-6}$  torr. Thus, the pyrolysis was conducted at low pressures and short contact times, and the products must travel only a few mm from the furnace exhaust port before being quenched.

Each pyrolysis run lasted 2 hours with inlet pressures of CIT of  $10^{-2}$  to  $10^{-1}$  torr (indicated at a distance of 93 cm from the furnace) and with furnace temperatures at  $320^{\circ}$  to  $380^{\circ}$ . Upon controlled warm-up, the quenched products vaporized and travelled less than 8 cm with no associated warming before controlled energy electron bombardment in the source. The principle products of pyrolysis are shown in Table 1, and each species was also observed in the

Table 1. Pyrolysis Products and Appearance Temperatures

<u>Compound</u>	<u>Temperature (<math>^{\circ}\text{C}</math>)</u>	<u>Relative Quantity</u>
CO	-196	large
$\text{C}_2\text{H}_2$	-155	medium
$\text{CO}_2$	-145	small
$\text{C}_4\text{H}_6$	-120	small
$\text{C}_4\text{H}_4$	-105	large
$\text{C}_6\text{H}_6$	-90	large
$\text{C}_8\text{H}_8$	-80	medium

earlier flash photolysis of CTT.<sup>3</sup> At  $-105^{\circ}$ , a large peak at  $m/e$  52,  $\text{C}_4\text{H}_4^+$ , and a small peak at  $m/e$  54,  $\text{C}_4\text{H}_6^+$ , were observed. Continuous pumping at  $-110^{\circ}$  for 6 hours failed to completely remove  $\text{C}_4\text{H}_6$ . The  $\text{C}_4\text{H}_6$  was identified as 1,3 butadiene and the mass spectrum of  $\text{C}_4\text{H}_4$  reported here (see Table 2) was obtained by subtracting the mass spectrum of 1,3 butadiene from the observed total mass spectrum at  $-105^{\circ}$ .

The isomers of cyclobutadiene, butatriene and vinylacetylene, have been prepared and each exhibited both a different mass spectrometric pattern and a different ionization potential as shown in Tables 2 and 3. To avoid possible misinterpretation from temperature effects, the ionization potentials of cyclobutadiene, vinylacetylene, and butatriene were determined at  $-100^{\circ}$ ,  $-108^{\circ}$ , and  $-90^{\circ}$ , respectively. These ionization potentials were also calculated using a semi-empirical SCF treatment recently developed by Dewar and Klopman.<sup>5</sup> The experimental and theoretical results are summarized in Table 3.



Table 2. TOF Mass Spectra of  $C_4H_4$  Isomers at 70 eV

<u>m/e</u>	<u><math>C_4H_4</math> from Pyrolysis of CIT</u>	<u>Butatriene</u>	<u>Vinylacetylene</u>
52	100%	100% (100%) <sup>a</sup>	100% (100%) <sup>b</sup>
51	59	70 (72-80)	56 (50.2)
50	51	51 (54)	49 (41)
49	17	26 (24)	19 (13)
48	1	8 (--)	8 (2.8)
39	5	1 (--)	1 (0.85)
26	26	18 (21.2)	12 (11.0)

(a) Measured with a magnetic mass spectrometer (CEC, model 21-103), W. M. Schubert, T. H. Libbicoet and W. A. Lanka, *J. Am. Chem. Soc.* **76**, 1929 (1954). Additional peak at m/e 53 of 14.7-22.2 per cent evidently arises from reaction during inlet.

(b) Measured with a magnetic mass spectrometer (CEC, model 21-101), Selected Mass Spectral Data, API Research Project 44.

Table 3. Experimental and Theoretical Ionization Potentials for  $C_4H_4$  Isomers

<u>Isomer</u>	<u>Experiment</u>	<u>Theory</u> <sup>a</sup>
Cyclobutadiene	9.55	8.9
Vinylacetylene	9.9 (9.9 <sup>b</sup> )	9.42
Butatriene	9.25	8.99

(a) Calculated using a semi-empirical SCF MO treatment developed by M.J.S. Dewar and G. Klopman, *J. Am. Chem. Soc.* **89**, 3089 (1967)

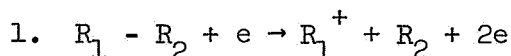
(b) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957, p. 261.

The ionization potentials at  $m/e$  52, 78 and 104, presumably  $C_4H_4$ ,  $C_6H_6$ , and  $C_8H_8$ , respectively, were determined from the low temperature evolved gases by the linear extrapolation method using ionization efficiency curves recorded directly from the electrometer using a Hewlett-Packard (Model 700/AR) X-Y plotter. The observed IP of  $C_8H_8$  was 9.1 eV, and since the value for cyclo-octatetraene is 8.6 eV,<sup>6</sup> the  $I(C_8H_8)$  observed here is postulated as cyclobutadiene dimer. The mass spectrum and ionization potential at  $m/e$  78,  $C_6H_6$ , are in agreement with that of benzene. The formation of benzene in the pyrolysis can occur by the reaction of cyclobutadiene and acetylene or by the polymerization of acetylene at these pyrolysis temperatures ( $320^\circ$  to  $380^\circ$ ). Benzene was in fact observed upon passing pure acetylene through the furnace at  $380^\circ$ .<sup>7</sup> The reaction of cyclobutadiene and acetylene to form Dewar benzene and then benzene itself has been suggested by Pettit.<sup>8</sup>

From these comparisons of the mass spectra and ionization potentials of the  $C_4H_4$  species, and from the formation of benzene and cyclobutadiene dimer, we conclude that cyclobutadiene was produced from the pyrolysis of CIT and quenched as a compound which is stable and probably isolable below about  $-90^\circ$ . We feel that this constitutes the most definitive study of this long-sought molecule that has appeared.

B. Three Carbon Strained Ring Compounds. - As discussed in previous reports, a major effort of our work has been to apply the techniques of cryochemistry to the synthesis and study of a family of small, 3-carbon strained ring compounds: cyclopropene, cyclopropanone, and cyclopropenone. These compounds, because of their strained structure, are all highly reactive, and they exhibit only a fleeting existence at room temperature while functionally serving as reaction intermediates. We have now shown that they can be isolated and stored indefinitely at low temperatures. We have synthesized these compounds and studied their molecular energetics by the use of cryogenic inlet systems adapted to a mass spectrometer.<sup>4</sup> From the measurement of ionization and appearance potentials of the compounds and fragments, we wanted to calculate heats of atomization, bond dissociation energies and ring strain for comparison with similar quantities obtained from theoretical calculations.

Energetic data from the measurement of appearance potentials of fragment ions are based on the following type reaction:

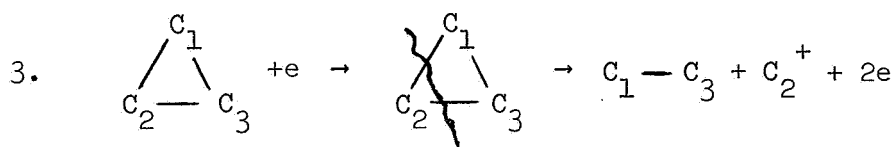


and equation:

$$2. \quad \text{A.P.}(R_1^+) = \Delta H_r = \Delta H_f^O(R_1^+) + \Delta H_f^O(R_2) - \Delta H_f^O(R_1 - R_2) + E^* \\ = D(R_1 - R_2) + R_1 + E^*$$

where:  $R_1$  - group of atoms bonded to another group,  $R_2$   
 $\text{A.P.}$  - mass spectrometrically measured appearance potential  
 $\Delta H_f^O$  - heat of formation  
 $E^*$  - excess energy of any fragment (includes translational, vibrational and rotational)  
 $D(R_1 - R_2)$  - bond dissociation energy.

In the case of ring compounds, fragmentation requires that two bonds be broken, and we wanted to study and interpret this rather more complex phenomenon, i.e.,



The preliminary interpretation of the data from the first compound investigated, cyclopropanone, proved to be inconclusive, and hence, a critical error analysis of expressions like Equation 2 had to be undertaken with compounds previously studied and interpreted by other workers in the mass spectrometric field. Possible sources of errors to be investigated were:

- (a) accuracy of A.P.
- (b) choice of fragmentation process and products
- (c)  $\Delta H_f^0$  of fragment, usually a number from the thermochemical literature
- (d) ionization and appearance potential values for both ground states and excited states
- (e) excess energy of fragments (translational and vibrational)

Excess energies of the fragment ions were studied by the method of Franklin.<sup>9</sup> This method is based on the theory and fact that fragment ions with a thermal distribution of velocities will exhibit a mass spectrometric peak shape which reflects the one-dimensional spread in velocities of the fragment ion after ionization. The width of each peak is directly proportional to the square root of ion mass and temperature. Any deviation from the standard width at room temperature is related to a change in ion temperature from which one can calculate the translational energy of the ion fragment and the translational energy of the neutral fragment. Franklin has further shown that this total excess translational energy is a definite fraction of the total (translational, rotational, and vibrational) excess energy.<sup>10</sup>

There is some doubt as to whether a particular ion observed in the mass spectrometer is a ring or an open structure. Since these unusually reactive cryogenic species presumably polymerize through a free radical structure, several LCAO-MO-SCF computer programs are being used to predict whether the ionization potentials of these various species differ enough energetically to be detected by a mass spectrometric measurement. Also, in the simultaneous breaking of two ring bonds, each fragment would initially be produced as an excited diradical, the energy of which may be calculable. Presently, only the computer programs limited to H and C are working correctly,<sup>5</sup> and data on cyclopropene are discussed later. Additional computations on C, H, and O molecules should be available soon.

### (a) Cyclopropane

Cyclopropane was investigated because it is similar to our unusual cryogenic molecules and because previous work on its energetics was available.<sup>11</sup> Appearance potentials of the fragments were measured and processes were chosen that came closest to being energetically consistent as described by Equation 2. Later work<sup>10</sup> showed that some of the ions possessed considerable excess energy and, then, that the processes chosen in the previous work were incorrect. Cyclopropane exhibited a variety of shapes of ionization efficiency curves which could be classified as to their value in energetic deductions.

Ionization potentials are obtained by comparing the unknown ionization efficiency curves to those of known standards. The shapes of unknown fragments usually fall distinctly into one of two classes: (1) they are nearly identical in shape with the standard, or (2) they possess a much longer initial curved tail. For the first type, any method of comparing the unknown and calibrating curves can be used with good results. The second type of curve is caused by more than one process contributing to the formation of the ion, and the overall resulting curve is the arithmetic sums of these individual processes. For a many-process ionization, the overall curve will have a long, shallow curve. This type of curve is impossible to compare to a standard and cannot be used to deduce energetic quantities. But, if the overall curve arises from only a few processes, it may have a long, but steep, curved tail. This case can be handled by the method of initial breaks.

With accurate appearance potentials and excess energies in hand, the  $\Delta H_f$  of cyclopropane was calculable from data on three ions, and it was shown that the products were not present as diradicals, but in their ground states. This molecule, then, provided a foundation to discuss the energetics of other cyclic compounds.

### (b) Cyclopropene

Cyclopropene slowly polymerizes at dry ice temperature ( $-78^\circ$ ). We synthesized this molecule by the reaction of allyl chloride with sodium amide, under conditions where the unstable cyclopropene could readily escape from the reaction mixture and be immediately trapped at  $77^\circ\text{K}$ .<sup>12</sup> The final product was purified by simple trap to trap distillation. This molecule was

investigated using both the low temperature inlet system (wherein the molecule was kept at  $-140^{\circ}$  until analyzed) and at room temperature. Mass spectra and appearance potentials measured at both temperatures appeared to be equivalent. This indicated that if the ring opened or a diradical formed upon warming, that it did so in only such small quantities that the product was energetically undetectable. All fragment ions were formed with little or no excess energies. But no fragments had a satisfactorily shaped curve to measure the appearance potential accurately. This is shown in Table 4 where all calculated  $\Delta H_f^{\circ}$  for

Table 4. Mass Spectrometric Data on Cyclopropane and Cyclopropene

Fragment m/e	I.P. (e.v.) or A.P.		Excess Energy		$\Delta H_f^{\circ}$ <sup>a</sup>			Curve	
	This Work		Lit.	Kcal./Mole.		Kcal./Mole.		Shape	
						This Work	Lit.		
	Exp.	Theory	Exp.	This Work	Lit.	Exp.	Theory	Exp.	This Work
42 (Parent)	10.3		10.2			1		13	Good
27	13.7		13.5	30		5			Long Tail
26	14.0		13.6	15		21			Long Tail
15	16.0		16.9	15		-40			Long Tail Shallow
14	18.5		18.8	90	120	15			Long Tail
40 (Parent)	9.8	9.7	9.9				41	67	Good
39	11.0		11.1						
27	13.5			0		100			Long Tail Shallow
26	16.4			0		-10			Long Tail Shallow
15	16.0			0		0			
14	15.0			15		77			

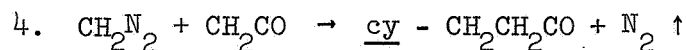
(a)  $\Delta H_f^{\circ}$  of parent as calculated from experimental A.P. of fragment ion using Equation 2.

cyclopropene are in considerable error. Note the good results for the I.P. of cyclopropene as calculated by the previously discussed computer program.

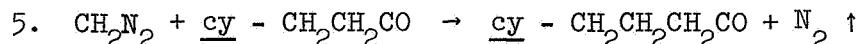
To test the temperature stability of the molecule, samples were thermostated at constant temperatures, then quenched to 77°K, and then warmed to determine whether the molecule had been destroyed and whether there were any gaseous decomposition products. The soak-temperatures ranged from -140° to room temperature and the product was stored under vacuum. We found no decomposition products, but a polymer which was noticeably formed only at about room temperature. In fact, a one-week room temperature exposure did not completely destroy cyclopropene as analysis showed both the molecule and a high molecular weight compound (m/e 80) which appeared to be the dimer. Thus, the compound appears to be much more stable than anticipated from other work. The polymer appeared to be a white waxy solid which smears upon contact at room temperature. The polymer was heated to near 300°, but it remained stable and showed no decomposition accompanied by off-gas evolution. The polymer was soluble in benzene, slightly soluble in gasoline, and insoluble in water, acetone, and methanol.

#### (c) Cyclopropanone

Cyclopropanone is a small ring compound that has been often proposed as a reaction intermediate, and at the time this work was begun, the species had never been isolated. We used a direct approach to its synthesis using the reaction of diazomethane with ketene.



Room temperature synthesis attempts have always yielded the butanone which was viewed as resulting from further reaction of diazomethane with cyclopropanone.



Diazomethane and ketene were prepared, purified, and characterized mass spectrometrically. The reaction was carried out in a cooled, evacuated trap by arranging, at liquid N<sub>2</sub> temperatures, a condensed ring of diazomethane

above a solid ring of ketene (in great excess). By then plunging the trap into a liquid refrigerant at  $-150^{\circ}$ , the solid yellow diazomethane became a viscous liquid which slowly ran down into and reacted with the now also liquid ketene producing a white solid and a volatile gas. The product gas was monitored mass spectrometrically and was identified as  $N_2$ . The rate of evolution of off-gas was constant with time, supporting the idea of a concentration independent, liquid-liquid reaction on the wall of the vessel.

After the excess reactants (which were proven to be entirely ketene) were removed by warming, the solid was transferred to the cryogenic inlet system where it was warmed and product peaks at  $m/e$  56 and  $m/e$  70 were studied at  $-90^{\circ}$  and  $-75^{\circ}$ , respectively. The relative volatilities of the two compounds allowed then to be separated sufficiently to obtain their mass spectra and energetic values. The vapor pressure, mass spectra, and energetic values of the heavier species were essentially<sup>13</sup> the same as those obtained in this laboratory from a pure sample of cyclobutanone (K & K Laboratories, Inc.). Likewise, the data for the lighter product were identical to that reported for cyclopropanone by Shaaafsma, et al.<sup>14</sup> Both cyclopropanone and cyclobutanone yield the same ions upon electron bombardment revealing their similar structure. On the basis of these data, we concluded that cyclopropanone had been isolated.

We also studied cyclopropanone at room temperature, and similar to cyclopropene, obtained the same I.P. for the parent indicating no major change in structure due to warming. However, this proved to be a very inefficient operation as most of the sample (greater than 95%) was polymerized, and the sample barely lasted long enough for the study.

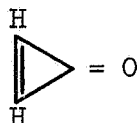
We have studied the temperature stability of this molecule by the same techniques as discussed under cyclopropene. This molecule is much more reactive than cyclopropene. Some polymerization was apparent at  $-90^{\circ}$ , a temperature at which cyclopropanone exerts little vapor pressure. It is difficult to tell whether the compound is a liquid or a solid at this temperature. Because of the localization of the polymer at the site where it was condensed as a solid, it appears that the polymerization reaction is at least begun, if not completed, as a solid or liquid before it reaches the vapor phase. Although a one-hour room temperature soak completely destroyed the cyclopropanone, no volatile decomposition products were observed. The polymer was a



white powder which, when heated to 200<sup>0</sup>, proved to be thermally unstable. The first product observed was m/e 56 which was interpreted as trapped cyclopropenone and not as polymer decomposition. Then heavier, but unidentified, products were observed. The polymer was soluble in benzene, slightly soluble in gasoline, somewhat soluble in acetone and alcohol, and not soluble in water. The original appearance potentials are now being reinvestigated in terms of what was learned from other cyclic compounds. Also, the computer calculation of the I.P. and  $\Delta H_f$  are now underway.

(d) Cyclopropenone

Cyclopropenone,

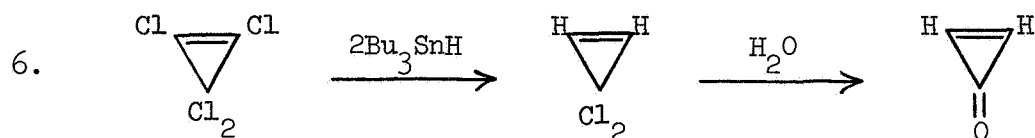


is a highly strained, small ring system that appears to possess considerable conjugative stabilization. Studies with the substituted molecule date from 1959, and compelling, but not absolutely conclusive, evidence for the synthesis of the parent ketone has appeared.<sup>15</sup> The original synthesis yields the ketone in aqueous solution, but attempts to isolate the substance, in work done by different research groups, whether by removal of the solvent by distillation, or by vapor phase chromatography under a variety of conditions have failed. Cyclopropenone is lost by polymerization just as is true of the hydrogenated analog, cyclopropanone.<sup>13</sup> Although the olefin appears to be more stable than the saturated compound, it cannot be kept in water solution as it hydrolyzes to form acrylic acid.<sup>15</sup>

Both of these ketones are interesting cryochemical systems. The cyclopropenone is particularly interesting in view of the failure of standard techniques in attempts to isolate the substance during the almost two years since its initial identification. The lack of published literature on the molecule since then also casts some doubt on its existence. The cryochemical equipment and procedures that have been developed in this laboratory are being applied to the isolation, energetics, and reactivity questions surrounding

this molecule. In view of the equivocal data, even with the great interest in the past of many investigators, it may well be that the techniques of cryo-chemistry may be the only way to effectively study this molecule.

The original apparent synthesis by Breslow and Ryan of cyclopropenone consisted of the reaction of tetrachlorocyclopropene with two equivalents of tri-n-butyltin hydride at room temperature in paraffin oil to produce a volatile mixture of mono-, di-, and tri-chlorocyclopropenes. This mixture of chlorinated products is taken up in  $\text{CCl}_4$ , then hydrolyzed with cold water to give an aqueous phase solution of the cyclopropenone. This sequence of reactions is as follows:



Our first attempt to reproduce this original synthesis was proved successful when both the dichlorocyclopropene and cyclopropenone were identified by nmr analysis. This preparation was done on a small scale and the purity was quite poor. Later, by utilization of mass spectrometric and infrared analysis, we were able to better control the preparations, and we obtained improved yields and much higher purity than in the first attempt. Tetrachlorocyclopropene can be kept indefinitely at room temperature.  $\text{Bu}_3\text{SnH}$  will react with air but it can be kept under argon sealed from air at room temperature. Dichlorocyclopropene, on the other hand, is itself a cryochemical which must be kept below  $-70^\circ$  or it is lost by polymerization. At room temperature, dichlorocyclopropene, within seconds, will begin to turn from a clear white liquid to yellow, and then steadily darken to a deep brown.

The original preparation of cyclopropenone resulted in a water solution. Trying to separate this solution by slowly warming from  $-196^\circ$  to room temperature under vacuum and immediate analysis by the mass spectrometer proved unsuccessful. A dominant peak at  $m/e = 19$  ( $\text{H}_3\text{O}^+$ ) suggested that cyclopropenone might have hydrolyzed to acrylic acid as it is known to do. Also, to vaporize the solvent water, the solution must be heated to a temperature at which the ketone would rapidly polymerize. Cyclopropenone is known to polymerize above  $-20^\circ$ . A polymer is formed during the slow warming but we cannot say definitely

it is from cyclopropenone as it could also be from unreacted dichlorocyclopropene. These data prove water to be an undesirable solvent.

The ketone can also be synthesized in acetonitrile and perhaps other solvents. We are attempting to find a more suitable solvent in which to perform the hydrolysis of the dichlorocyclopropene and which will, in turn, enable the product to be separated. An obvious choice of solvent is one greatly differing in volatility. Performing the reaction at atmospheric pressure in a non-volatile solvent, and following this by vacuum pumping may allow the ketone to be evolved as a free gas. Conversely, a very volatile solvent may be evaporated at a low enough temperature to leave behind an unpolymerized product.

According to Ryan,<sup>16</sup> the hydrolysis reaction in pure dichlorocyclopropene results in a black polymer, liberating CO gas. But this same reaction, slowed and controlled by carrying it out at cryogenic temperatures, may possibly yield the unpolymerized ketone.

We plan to carry out the above described experiments in the next few weeks. Results from the computer calculation of the most stable structure for cyclopropenone should also be available within the next few weeks.

### III. FUTURE PLANS

The nature of our continued research with the above series of small strained-ring systems has already been described. Several new systems seem particularly promising, and hence, some expansion in scope will occur during the ensuing year.

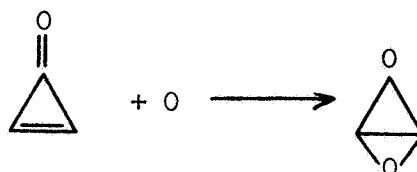
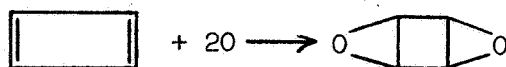
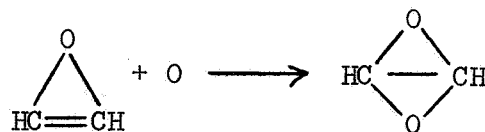
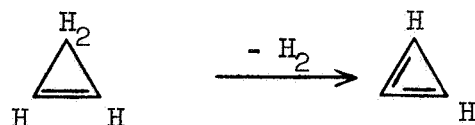
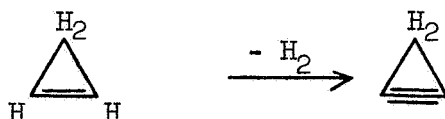
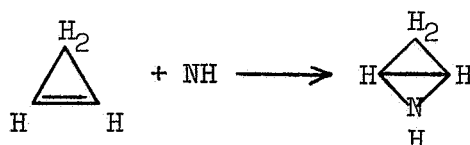
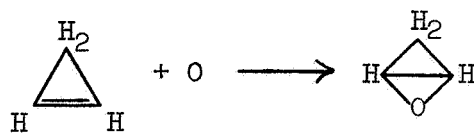
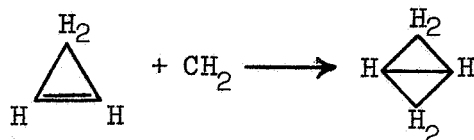
(a) Oxirene. Although we have been unable to perform any definitive experiments, we propose to continue work toward the synthesis of this highly strained, unsaturated, heterocycle,



The most promising approach still seems to be the addition of  $^1\text{D}$  excited O atoms to outline at low temperatures.

(b) Cryogenic Reactions of New Molecules. Successful synthesis of the unusual and reactive compounds of Chapter II opens the door to exploration of their chemistry. For example,

7.

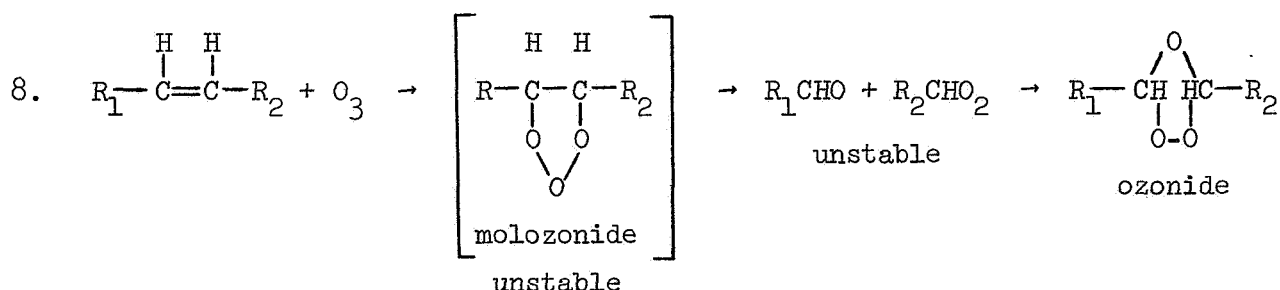


All of these suggested product molecules are presently unknown and may well be non-existent, even at cryogenic temperatures, in view of high strain in the bonds. But these typical examples of cryochemical reactivity, as well as many others that could be written, seem logical and interesting follow-ups to our successful syntheses of the required (and previously unavailable) unusual cryochemical reagents.

(c) Ozonides. Ozone may well be an important cometary constituent as well as a constituent of the atmospheres or surfaces of the Jovian planets. It is also a highly reactive cryogenic liquid whose chemical characteristics are still rather obscure.

In earlier reports on this NASA program, we reported rather unsuccessful attempts to confirm the much debated synthesis of hydrogen superperoxide,  $H_2O_4$ , from the reaction of atomic hydrogen with liquid  $O_3$  at  $77^\circ K$ . These experiments were plagued by frequent and ill understood explosions. We propose to continue these studies utilizing our improved technique and equipment that has been developed in the meantime.

Ozone is believed to react with olefins to form ozonides via the formation of an unstable transitory adduct called molozonide, but such a species has never been directly observed.



We propose to study the above reaction at very low temperatures with a number of simple unsaturated hydrocarbons (for example, ethylene, acetylene, dicyanoacetylene, etc.) with the objective of isolating the molozonide (if it exists) or any other reactive intermediate. With success here, energetic, stability, and reactivity studies will be conducted in the usual manner.

(d) Nitrogen Compounds. A family of N-H compounds may be postulated: triazene ( $\text{H}_2\text{N}-\text{N}=\text{NH}$ ), triazane ( $\text{H}_2\text{N}-\text{NH}-\text{NH}_2$ ), tetrazene ( $\text{H}_2\text{N}-\text{N}=\text{N}-\text{NH}_2$ ), etc. In earlier reports on this NASA program, we have shown that the simplest dinitrogen compound, diimide ( $\text{N}_2\text{H}_2$ ), may be made from the cryogenically quenched atomic oxygen-ammonia flame. One may also postulate that "Rice's blue stuff" quenched from pyrolyzed  $\text{HN}_3$  may be a cyclic trimer,  $(\text{NH})_3$ , or either ozone-like since NH is isoelectronic with O. Finally, it was also recently shown in low temperature matrix experiments that atomic fluorine will abstract hydrogen from  $\text{HN}_3$  to yield the  $\text{N}_3$  radical.

We propose to study the reactions of NH (from  $\text{HN}_3$ ), and  $\text{N}_2\text{H}_3$  (from hydrazine) and  $\text{N}_2\text{H}_2$  (from  $\text{O} + \text{NH}_3$  flame) in attempts to form three and four membered cyclic and acyclic compounds of this family. We also propose to study the formation of cyclic  $\text{N}_6$  from the dimerization of two  $\text{N}_3$  free radicals. The molecular energetics, the region of thermal stability and the identification of the reaction or decomposition products from all of these studies will be accomplished with the aid of the cryogenic mass spectrometers in the usual way.

(e) Cyanogen Azide. Cyanogen azide,  $\text{N}_3\text{CN}$ , is an unstable and highly reactive molecule which has recently been synthesized, and it has been the object of several reactivity studies.<sup>17</sup> Upon pyrolysis, it yields  $\text{NCN}$  radicals which then dimerize to form  $\text{NC}-\text{N}=\text{N}-\text{CN}$  which is itself an orange-red, highly reactive, volatile compound.

We propose to make a series of exploratory studies of the chemistry of cyanogen azide at very low temperatures with a view toward the development of information pertinent to the origin of CN emission from comets. For example, the discovery of an H-C-N-O compound in which the cyanogen group was only weakly bonded (say  $D(\text{M-CN}) < 1 \text{ ev}$ ) would be a good candidate species for low intensity photolysis.

#### IV. ADDITIONAL INFORMATION

After careful arrangements to insure efficiency and continuity, NASA approved a proposed leave-of-absence to allow the Principal Investigator to serve the first nine months of 1969 as a visiting professor in the Chemistry and Chemical Engineering Division at the California Institute of Technology.

His salary will be paid jointly by Caltech and Georgia Tech, together with a very small contribution from this NASA grant. During this leave-of-absence, the Georgia Tech Foundation has made funds available to allow monthly return visits by Dr. McGee for consultations with his research students and for the continued supervision of this NASA research program. Dr. McGee's work at Caltech will involve seminars, lectures, consultations with Research Fellows, etc. on matters of the same or very closely related areas of research as are now underway in his laboratory at Georgia Tech. It should be possible to enlist at least one Post-Doctoral Fellow at Caltech who would begin work at Caltech and then move on to the Georgia Tech laboratories at an appropriate time.

Joint investigations are also being developed. Already, an experiment with cyclopropanone immersed in liquid nitrogen has been transported from Atlanta to Pasadena. Unique facilities and expertise at Caltech, combined with long experience in cryochemistry at Georgia Tech, permit broader and more definitive studies than would be possible at either Institute alone. We anticipate and are working toward long-term collaborative research programs.

Other campus functions of the Principal Investigator include service on a Board responsible for the administration of a large (\$300,000/year) NASA Sustaining University Grant and on a small committee appointed by the Chancellor of the University System of Georgia to advise him in the selection of a new President for Georgia Tech. Dr. McGee has been named Meeting Program Chairman of the 67th National Meeting of the American Institute of Chemical Engineers to be held in Atlanta in February 1970. In this position he is responsible for the entire technical program of this national Institute meeting.

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